Chapter 7 - Conclusion

The potential for processing metals like plastics inspired much of the research of this thesis. Some of the most important inventions and discoveries made in the course of pursuing that goal are listed below.

1. ZrTiBe + ETM increases GFA (no LTM required) (Ch2).
2. ZrTiBe + ETM alloys can be as light as Ti and as strong as tool steel (Ch2).
3. ZrTiBe alloys can be cast amorphous in 1 - 6mm diameter rods (Ch3).
4. Substitution of Be with small amounts of LTM in ZrTiBe alloys exhibiting large ΔT values leads to alloys with even larger ΔT values until other phases are formed with too much LTM (Ch3).
5. Cu is the most effective element at increasing ΔT of ZrTiBe + Me alloys (Ch3).
6. The alloy with the largest ΔT in the literature prior to my entry into grad school in 2005 was $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ with ΔT = 135 °C. The current record holder. $Zr_{35}Ti_{30}Be_{27.5}Cu_{7.5}$, has ΔT = 165 °C and was found in the course of research for this thesis (Ch3).
7. Investigation of the viscosity and TTT properties of $Zr_{35}Ti_{30}Be_{27.5}Cu_{7.5}$ revealed that for TPF processes requiring 60 - 300 s, this newly discovered alloy provides 10x lower processing viscosity than the other well known alloys for TPF (Ch4).
8. TTT data and η(T) data can be combined to give valuable processing information for TPF processes. The resulting ηTT plots tell how long one can process at a desired viscosity before crystallization (Ch5). This concept will be further discussed later in the conclusion.

9. The discovery of $Zr_{35}Ti_{30}Be_{27.5}Cu_{7.5}$ with $\Delta T = 165$ °C allowed injection molding of a metallic glass to be demonstrated for the first time (Ch5).

10. The discovery of bulk glass formers in the ZrTiBe system facilitated a better understanding of the SCLR of these alloys and allowed for a clear observation of two relaxation phenomena in the SCLR that is likely related to the phase separation observed in Vitreloy alloys upon annealing in the SCLR (Ch6).

11. ZrTiBe + Me compositions exhibit very low corrosion rates in 50% w/w NaOH, 0.6M NaCl, and 10x PBS (A1).

12. ZrTiBe + Me compositions have corrosion rates varying from 50 MPY to 10^7 MPY in 12M HCl and show a log linear relationship with half cell potential (SHE) (A1).

13. ZrTi based Be bearing alloys show evidence of good biocompatibility (A2).

14. We discovered ZrTiBe + Me compositions with 10x better corrosion resistance in ocean water than other Zr based BMG alloys in the literature and other crystalline alloys commonly used in marine environments (A3).

15. Corrosion fatigue properties are similar to other Zr based BMG alloys despite improved corrosion resistance in 0.6M NaCl (A3). This makes the use of Zr based BMG alloys unlikely in load bearing applications in saline environments like the ocean or the human body.

My optimistic hopes for broad ranging application of these materials in the orthopaedics industry compelled me to learn about corrosion, take a cell culture class, explore pertinent literature on biocompatibility, and study fatigue of materials. That investigation culminated in the discovery of the material's terrible corrosion fatigue properties. It is disappointing to dream about endless possibilities and then find that they will not materialize as I had imagined. However, the excitement, discovery, and learning that ensued more than compensated for the occasional disappointment.

Challenging aspects of this research have yet to be fully explored. Some of this research I hope to participate in and some may keep future grad students investigating and learning.

7.1 Future Research Directions

We need to determine if phase separation is happening in the ZrTiBe system. As discussed in Chapter 6, SANS is difficult with these samples due to limited GFA so SAXS is our best option. Discussion with scientists at Argonne National Laboratory is underway and if a length scale of phase separation can be found, future microscopy attempts may be more fruitful. If no phase separation is discovered then an alternate analysis of the physics behind the two T_g phenomenon observed in the SCLR of these alloys could be explored.

While we were unable to find an alloy that would work as a drop-in replacement for plastics in TPF processes, we simplified the way we think about TPF with ηTT plots and found an alloy that has 10x lower processing viscosity than the previous best alloys for conventional TPF processes requiring 60 – 300 s. An important contribution of this work to the field of metallic glasses was the discovery that new TPF processes must be completed in well under 60 s to achieve optimum formability. A major difficulty in pursuing my research was having to wait while material heated slowly in a barrel as it moved toward crystallization. This difficulty is depicted in Figure 7.1.

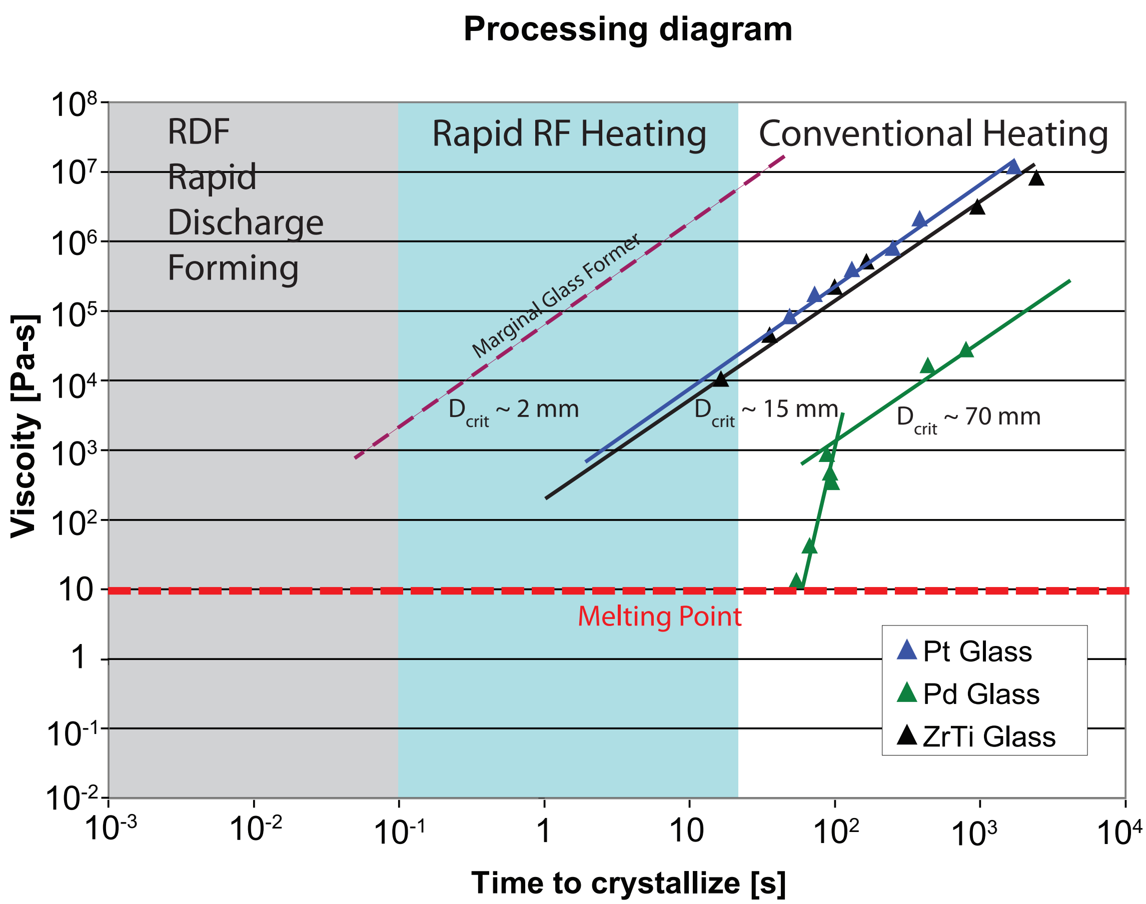

Figure 7.1: Heating and forming times achievable using rapid discharge forming, RF heating, and conventional heating depicted along the x axis. ηTT data for a marginal glass former is schematically represented with the dashed line. ηTT data for the Pd alloy is sketchy because it is estimated from constant heating experiments in [1-2] but shows a change in slope as the melting temperature is approached. ηTT data for Pt alloy found in [2-3], and for the Zr alloy in [2, 4].

New TPF ideas are being pursued in the Johnson group to address the need for faster processing and mainly faster heating. One way to rapidly heat metallic glass is by using RF heating. An alternating current is placed on a solenoid and the resultant eddy currents induced in near by metallic material to counter the changing magnetic flux causes resistive heating. This method can heat a sample in under a second and with an appropriate force, the forming could be completed in less than 10 seconds depending on part geometry. The processing window accessible using this method is shown on Figure 7.1 and labeled RF.

Another method already being explored in the Johnson group is abbreviated RDF, rapid discharge forming (not radial distribution function). It is well described in a patent application entitled "Forming of Metallic Glass by Rapid Capacitor Discharge" [5]. This method takes advantage of the unusual resistive properties of metallic glasses. Crystalline metals usually have increasing resistances with increasing temperature. This causes crystalline material to develop hot zones near a contact with a capacitor. Metallic glasses have decreasing electrical resistance with increasing temperature. If a hot zone begins to develop in a metallic glass, the local resistance will decrease and cause the cooler regions to dissipate more of the energy resulting in uniform heating of a sample. This heating method can bring a metallic glass to a temperature in the SCLR in milliseconds. The RC time constant is the governing time scale and material can be taken all the way to the melting temperature with an appropriate sample size to capacitor energy ratio allowing access to the entire SCLR upon heating. This method theoretically allows any process viscosity up to the melt viscosity to be accessible for processing if the flow and cooling can happen quickly enough to bypass crystallization. Heating is no longer the limiting factor in process time using this processing method. This processing window is shown on Figure 7.1 and labeled RDF.

The ability to form parts with thin sections and complicated geometries is limited by the time available to heat, form, and cool them amorphous. One bonus to development of rapid heating technologies combined with large ΔT alloys is the ability to spend much longer times in the forming step by minimizing the time required for heating.

Parts exceeding the critical casting thickness of the alloy could even be created provided sufficient time exists to cool them in the SCLR and as demonstrated in Chapter 5, the parts resulting from TPF are more reliable than die cast parts and exhibit similar strengths with less scatter in strength.

The RDF and RF methods of heating allow alloys with smaller ΔT to be considered for TPF. Part geometries are likely more limited than larger ΔT alloys could achieve, but alloys exhibiting desirable properties but poor GFA would become much more useful. TTT diagrams are accessible upon heating to much higher temperatures using rapid heating methods than with previous experimental methods. The SCLR of most glass forming alloys could be thoroughly explored.

I wish to close with a special thanks to Dr. Johnson for creating a fantastic atmosphere of theory and experimentation. It was exactly the education I hoped for.

Chapter 7 References

[1] J. Schroers, W.L. Johnson, R. Busch, Appl. Phys. Lett. 77 (2000) 1158.
[2] W.L. Johnson, M.D. Demetriou, J.S. Harmon, M.L. Lind, K. Samwer, MRS Bull. 32 (2007) 644.
[3] B.A. Legg, J. Schroers, R. Busch, Acta Mater. 55 (2007) 1109.
[4] T. Waniuk, J. Schroers, W.L. Johnson, Phys. Rev. B 67 (2003) 184203.
[5] W.L. Johnson, M.D. Demetriou, C.P. Kim, J.P. Schramm, US Patent application #20090236017.